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(54) METHOD OF MANUFACTURING FINE METAL POWDER

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PATENT SPECIFICATION

(54) Title of the Invention: Method of Manufacturing Fine Metal Powder

(57) [Abstract]
[Problem] To provide a method of manufacturing a fine metal powder that does not require the use of large-scale equipment, allows extremely easy production of a very fine metal powder with uniform graininess, and does not require implementation of special measures against oxidation of the produced fine metal powder.
[Means for the Solution of the Problem] Production of a fine metal powder by heating metal alkoxides in a non-aqueous solvent.

[Claims]
[Claim 1] A method of manufacturing a fine metal powder by heating metal alkoxides in a non-aqueous solvent.

[Claim 2] The method of Claim 1, wherein said fine metal powder is made from such a metal as iron, cobalt, nickel, or from a more precious metal than iron, cobalt and nickel.

[Claim 3] The method according to Claim 1 or Claim 2, wherein said non-aqueous solvent is a polyhydric alcohol or liquid paraffin.

[Claim 4] The method according to any of Claims from 1 to 3, wherein said metal alkoxide has 1 to 4 carbon atoms.

[Detailed Description of the Invention]

[0001]
[Field of the Invention] The present invention relates to s method of manufacturing a fine metal powder, in particular, to a method suitable for easy production of a metal powder of extremely high fineness.

[0002]
[Description of the Prior Art] In accordance with conventional practice, a fine metal powder is normally produced by heating and reducing a metal alkoxide in a hydrogenous atmosphere.

[0003]

[Problems to be Solved by the Present Invention] Since a known method based on reduction of metal alkoxides in hydrogen is associated with heating in the presence of hydrogen, such a process requires the use of large-scale equipment. Furthermore, obtaining of a very fine powder by the known method with reduction in a gaseous phase is not an easy task since special countermeasures have to be undertaken against oxidation of the produced micropowder.

[0004] The present invention is aimed at elimination of the problems inherent in the prior art and provides an extremely easy method of manufacturing a fine metal powder of uniform graininess and without necessity of using special countermeasures against oxidation of the fine powder produced by the proposed method.

[0005]
[Means for the Solution of the Problem] Production of a fine metal powder by heating metal alkoxides in a non-aqueous solvent.

[0006] According to the method of the invention, the fine metal powder can be produced by merely heating metal alkoxides in a non-aqueous solvent. The heating temperature should not exceed 200°C. The process does not require the use of special equipment and is extremely simple. Furthermore, since the fine metal powder is produced in a liquid phase, it has uniform graininess and dimensions of particle below 100 nm. Since the fine metal powder is produced in a non-aqueous liquid and has no contact with the atmosphere, there is no need in implementation of measures for protection against oxidation.

[0007] According to the method of the invention, a fine metal powder can be easily produced from such a metal as iron, cobalt, nickel, or from a more precious metal than iron, cobalt and nickel.

[0008] A non-aqueous solvent suitable for the method of the invention may comprise is a polyhydric alcohol or liquid paraffin. Metal alkoxides having 1 to 4 carbon atoms are more suitable for the process.

[0009]

[Description of the Preferred Embodiments] The invention will now be described in more detail with reference to practical embodiments.

[0010] A metal alkoxide used as a starting material in the method of the invention can be produced by adding a metal having high tendency to ionization and high reactivity , such as, e.g., metallic sodium, to alcohol. As a result, a sodium alkoxide is produced. A compound prepared from a metal of the metal powder that is to be produced is added to the obtained sodium alkoxide, and the mixture is subjected to refluxing.

[0011] As an alcohol, it is preferable to use methanol, ethanol, isopropanol, n-butanol, or a similar lower monohydric alcohol with 1 to 4 carbon atoms. Although the following description of the method will relate only to metallic sodium as a metal reactive to the alcohol, it is understood that the method is not limited only to sodium and other metals such as lithium or an alkali-earth metals are also suitable for the invention. However, sodium is recommended as a substance that can be easily obtained and is easy to handle.

[0012] The compounds that facilitate (in the method of the invention with heating of a metal alkoxide in a non-aqueous solvent) production of a fine powder with grains smaller than usual, especially from such metals as iron, cobalt, nickel, or precious metals, i.e., from metals that show a tendency to ionization, may comprise metal compounds reactive to sodium alkoxides. These compounds may comprise iron, nickel, cobalt, copper, gold, platinum, palladium compounds, etc., e.g., chlorides, acetates, or oxalates of the above metals. It is important to note that when these compounds participate in the reaction, they do not generate water. Specific examples of the aforementioned compounds are given below.

[0013] Nickel Compounds, Such as Anhydrous Nickel Chloride, Anhydrous Nickel Acetate

If an anhydrous nickel chloride and anhydrous copper acetate are used, respective metal alkoxides can be produce in the below-given reactions by adding the aforementioned metal compounds to a sodium alkoxide:

[0014] 2Na alkoxide + $NiCl_2$ → 2NaCl + nickel alkoxide

2Na alkoxide + $Cu(CH_3COO)_2$ → $2CH_3COONa$+ copper alkoxide.

Sodium compounds, such as sodium chloride and sodium acetate that are by-product compounds of the reaction, can be removed, e.g., by solvent extraction.

[0015] A metal alkoxide produced by the method of the invention as described above is added to a non-aqueous solvent and is heated therein.

[0016] A non-aqueous solvent suitable for the above process may comprise polyhydric alcohols, liquid paraffins, or fatty acid glycerides. Polyhydric alcohols may be represented by ethylene glycol, propylene glycol, butadiol, dipropylene glycol, polyethylene glycol, etc.

[0017] Metal alkoxides added to non-aqueous solvents should be used in amounts from sufficient uniform distribution to partial dissolving in the non-aqueous solvent. In this case, heating may contribute to the formation of a more uniform reaction system. Normally, a metal alkoxide should be added in an amount of 200 to 500 g per 1 liter of the non-aqueous solvent.

[0018] The heating temperature may depend on the type of the metal alkoxide used in the process and on the heating time. Normally, the heating temperature is selected within the range of 130 to 180°C. If the temperature is below the lower recommended limit, a longer heating time will be required. If the heating temperature is selected in a higher portion of the 120-200°C range, the heating time can be reduced. In general, a desired fine metal powder can be obtained during 30 to 60 min.

[0019] The method of the invention makes it possible to produce a uniform fine metal powder with the particle size of 10 to 100 nm. The obtained powder can be efficiently used, e.g., as a catalyst for various chemical syntheses. High catalytic activity of the produced fine powder is achieved due to high specific surface inherent in a powder having small particle diameter.

[0020]

[Practical Examples] The invention will be further described with reference to specific practical examples.

[0021]
Practical Example 1

Nickel alkoxides shown in Table 1 were obtained by adding sodium metal to methanol, ethanol, isopropanol, and n-butanol, respectively. An anhydrous nickel chloride was then added, and the mixtures were subjected to refluxing. NaCl that comprised a reaction by-product was removed from the reaction system by washing with methanol. The obtained nickel alkoxides (23 g) were dispersed in 100 ml of ethylene glycol, and the dispersions were heated for 60 min. at temperatures shown in Table 1.

[0022] Upon completion of heating, the products were subjected to X-ray analysis. The results are shown in Table 1. The symbols used in Table 1 have the following meaning: [○] – fine nickel powder is formed; nickel alkoxide is not observed; [Δ] - fine nickel powder is formed; residual nickel alkoxide is observed; [X] fine nickel powder is not formed; nickel alkoxide remained unchanged.

[0023] The size of particles in the obtained fine nickel powder was determined by X-ray peak analysis and by measurements with the use of an electronic microscope. Irrespective of the type of the used alkoxide, in all cases the nickel powder particles had dimensions about 30 nm.

[0024]
[Table 1]

No.	Type of Nickel Alkoxide	Heating Temperature (°C)				
		60	90	120	150	180
1	Ni methoxide	X	X	X	X	○
2	Ni-ethoxide	X	X	X	Δ	○
3	Ni-isopropoxyde	Δ	Δ	Δ	Δ	○
4	Ni-butoxide	Δ	Δ	Δ	Δ	○

[0025] Practical Example 2
A copper ethoxide was produced by adding metallic sodium to ethanol, then adding anhydrous copper acetate, and removing the by-product CH_3COONa by washing with ethanol. The obtained copper ethoxide (21 g) was dispersed in 100 ml of ethylene glycol, and the dispersion was heated at 130°C for period of times shown in Table 2.

[0026] Dimensions of particles of the obtained fine powders were measured by the same methods as in Practical Example 1, and in all cases these dimensions were close to 50 nm.

[0027]
[Table 2]

No.	Duration of Heating (min.)					
	90	100	110	120	180	300
5	X	X	Δ	O	O	O

[0028] In Practical Example 3, a fine nickel powder was produced by the same method as in Practical Example 1, with the exception that liquid paraffin was used instead of ethylene glycol. Results of evaluation were obtained in the same manner as in Practical Example 1, and the obtained nickel powder had almost the same dimensions of particles as in Practical Example 1.

[0029] In Practical Example 4, a fine copper powder was produced by the same method as in Practical Example 2, with the exception that ethylene glycol was used instead of liquid paraffin. Results of evaluation were obtained in the same manner as in Practical Example 2, and the obtained copper powder had almost the same dimensions of particles as in Practical Example 2.

[0030]
[Effects of the Invention] As has been shown above, manufacturing of a fine metal powder by the method of the present invention does not require the use of large-scale equipment. The powder can be easily produced with uniform graininess of the microparticles. Furthermore, the method does not require the use of special countermeasures against oxidation of the produced powder, and therefore is advantageous industrial application.